Reactions of the electron-rich triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl, Br) with dioxygen Part II*. The synthesis and structural characterization of the complexes $ReOCl_3(dppmO)$ (dppmO = $Ph_2PCH_2P(O)Ph_2$) and $Re_2(\mu\text{-O})Cl_6(\mu\text{-dppm})_2$

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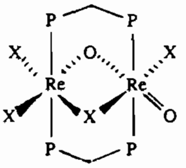
Abstract

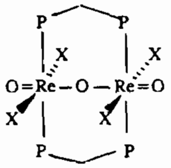
The compound $Re_2(\mu\text{-O})(O)_2Cl_4(\mu\text{-dppm})_2$ (**2a**), which has been prepared previously by the reaction of $Re_2Cl_4(\mu\text{-dppm})_2$ with O_2, reacts with further O_2 to form mononuclear $ReOCl_3(dppmO)$ (**3**), where dppmO represents the chelating $Ph_2PCH_2P(O)Ph_2$ ligand. Complex **3** can also be prepared by the reaction of **2a** with Bu^tOOH, H_2O_2 or *m*-chloroperbenzoic acid. The structure of **3** has been determined by single crystal X-ray crystallography. Crystal data for $ReOCl_3(dppmO)\cdot CH_2Cl_2$ at 20 °C: monoclinic space group $P2_1/n$ (No. 14), $a = 10.0440(8)$, $b = 15.821(1)$, $c = 18.082(2)$ Å, $\beta = 91.994(7)°$, $V = 2871.6(7)$ Å^3, $Z = 4$. The structure was refined by full-matrix least-squares to $R = 0.025$ ($R_w = 0.037$) for 3177 data with $I > 3\sigma(I)$. The dirhenium(V) complex **2a** can be protonated to give the μ-hydroxy bridged complex $[Re_2(\mu\text{-OH})(O)_2Cl_4(\mu\text{-dppm})_2]BF_4$ (**5**) upon treatment with $HBF_4\cdot Et_2O$. Complex **5** is deprotonated to reform **2a** by bases such as triethylamine. The dirhenium(IV) complex $Re_2(\mu\text{-O})(\mu\text{-Cl})(O)Cl_3(\mu\text{-dppm})_2$ (**1a**), which is a precursor to **2a** in the oxygenation of $Re_2Cl_4(\mu\text{-dppm})_2$, reacts with thionyl chloride to form the centrosymmetric corner-sharing bioctahedral complex $Re_2(\mu\text{-O})Cl_6(\mu\text{-dppm})_2$ (**4**), which is isostructural with its previously described osmium analogue. Crystal data for **4** at 20 °C: orthorhombic space group *Pbca* (No. 61), $a = 15.087(1)$, $b = 17.878(4)$, $c = 18.015(3)$ Å, $V = 4859(2)$ Å^3, $Z = 4$. The structure was refined by full-matrix least-squares to $R = 0.029$ ($R_w = 0.034$) for 2110 data with $I > 3\sigma(I)$.

Introduction

We have recently established [1, 2] that in the reactions of dioxygen with the triply bonded dirhenium(II) complexes $Re_2X_4(\mu\text{-dppm})_2$ (X = Cl or Br; dppm = $Ph_2PCH_2PPh_2$) multi-electron redox processes (4e and 6e) occur to form the compounds $Re_2(\mu\text{-O})(\mu\text{-X})(O)X_3(\mu\text{-dppm})_2$ and $Re_2(\mu\text{-O})(O)_2X_4(\mu\text{-dppm})_2$ whose structures are as represented below (**1** and **2**). In a subsequent study [3], we showed that **2a** can be reversibly converted to the tetraoxodirhenium(V) complex $Re_2(\mu\text{-O})_2(O)_2Cl_2(\mu\text{-dppm})_2$. We have now examined additional aspects of the reactivity of **1** and **2**, specifically that of the chloro complexes **1a** and **2a**, and in so doing have expanded further the chemistry of oxo complexes that contain the very stable $[Re_2(\mu\text{-dppm})_2]$ structural unit.



1a X = Cl
b X = Br



2a X = Cl
b X = Br

Experimental

Starting materials

The following dirhenium compounds were prepared by literature procedures: $Re_2Cl_4(\mu\text{-dppm})_2$ [4], $Re_2(\mu\text{-O})(\mu\text{-Cl})(O)Cl_3(\mu\text{-dppm})_2$ (**1a**) [1, 2] and $Re_2(\mu\text{-O})(O)_2Cl_4(\mu\text{-dppm})_2$ (**2a**) [1, 2]. The other reagents and solvents were obtained from commercial sources and were used without further purification. Solvents were dried prior to use.

Reaction procedures

Unless otherwise stated, all reactions were carried out under an atmosphere of gaseous N_2.

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*Part I is ref. 1.

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Synthesis of $ReOCl_3(dppmO)$ (3)

(i) Method A. A quantity of **2a** (0.040 g, 0.03 mmol) was dissolved in THF (6 ml) and the solution stirred in an open flask at room temperature for *c.* 30 h. At the end of this period the green solution was treated with an excess of diethyl ether (40 ml) to induce precipitation of the pale green complex. The product was filtered off, washed with diethyl ether (5 ml) and recrystallized from a CH_2Cl_2/diethyl ether mixture; yield 0.010 g.

A similar procedure can be used starting with complex **1a** (0.040 g, 0.03 mmol) in place of **2a**; yield 0.008 g.

(ii) Method B. A solution of **2a** (0.035 g, 0.026 mmol) in 5 ml of CH_2Cl_2 was treated with a small quantity of Bu^tOOH (0.4 ml of a 3.0 M solution in 2,2,4-trimethylpentane) and the mixture stirred at room temperature for 2 h. The pale green solution was then reduced in volume to 2 ml and an excess of diethyl ether (15 ml) added. The mixture was allowed to stand in the atmosphere for a few hours, and the pale green solid filtered off, washed with diethyl ether (5 ml) and dried under vacuum; yield 0.012 g (65%). *Anal.* Calc. for $C_{25.5}H_{23}Cl_4O_2P_2Re$ (i.e. $ReOCl_3(dppmO)\cdot 0.5CH_2Cl_2$): C, 40.76; H, 3.09. Found: C, 40.99; H, 3.19%.

This same procedure can be used with *m*-chloroperbenzoic acid (0.05 g, 0.290 mmol) or 30% H_2O_2 solution (0.1 ml) in place of ^tBuOOH. When complex **1a** is used as the starting material instead of **2a**, the product is still **3** although the yield is reduced (48%).

(iii) Method C. The reaction of **1a** (0.050 g, 0.038 mmol) with $NOPF_6$ (0.018 g, 0.105 mmol) in acetone (5 ml) was carried out at room temperature for 15 h and the volume of solution then reduced to *c.* 2 ml. The reaction mixture was worked-up by use of a procedure similar to that used in methods A and B; yield 0.018 g. The identity of the product was based upon its spectroscopic and electrochemical properties.

Synthesis of $Re_2(\mu\text{-}O)Cl_6(\mu\text{-}dppm)_2$ (4)

A quantity of **1a** (0.060 g, 0.046 mmol) was dissolved in 5 ml of CH_2Cl_2 and this solution was then treated with 0.04 ml of $SOCl_2$. The mixture was stirred for 15 h and an excess of diethyl ether (40 ml) added to precipitate a brown product. This was filtered off, washed with copius quantities of acetone to remove a gray–green impurity and then with diethyl ether (3×3 ml), and finally vacuum dried; yield 0.032 g (51%). *Anal.* Calc. for $C_{50}H_{44}Cl_6OP_4Re_2$: C, 43.83; H, 3.24; Cl, 15.53. Found: C, 43.00; H, 2.99; Cl, 15.66%.

Reaction of 1a with ferrocenium hexafluorophosphate

A mixture of **1a** (0.050 g, 0.038 mmol) and $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ (0.013 g, 0.039 mmol) was dissolved in 3 ml of deoxygenated CH_2Cl_2 and the reaction stirred at room temperature for 12 h. The resulting green solid was filtered off and washed with diethyl ether (15 ml) and vacuum dried; yield 0.038 g. *Anal.* Found (duplicate analyses on different preparative samples): C, 43.41, 43.54; H, 3.63, 3.40; Cl, 11.54%. The use of $(C_7H_7)PF_6$ or $(Ph_3C)PF_6$ in place of $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$ gave this same product.

The IR spectrum of this product showed no band between 1000 and 800 cm^{-1} that could be attributed to a $\nu(Re{=}O)$ mode. Its ^1H NMR spectrum (recorded in CD_2Cl_2) showed broad phenyl proton resonances between $\delta + 8.0$ and $+6.8$ but the $-CH_2-$ resonance of the dppm ligand was not located. A cyclic voltammogram on a solution of this material in 0.1 M TBAH–CH_2Cl_2 showed well-defined processes at $E_{1/2}(ox) = +0.60$ V, $E_{1/2}(red) = -0.51$ V and $E_{1/2}(red) = -1.69$ V versus Ag/AgCl; for the first two processes the ΔE_p values ($E_{p,a} - E_{p,c}$) were 70 and 80 mV, respectively, while for the reduction at -1.69 V, $\Delta E_p = 140$ mV.

Protonation of 2a to form $[Re_2(\mu\text{-}OH)(O)_2Cl_4(\mu\text{-}dppm)_2]BF_4$ (5)

A suspension of **2a** (0.040 g, 0.030 mmol) in 4 ml of CH_2Cl_2 was treated with 0.05 ml of $HBF_4\cdot Et_2O$. The clear green solution was stirred at room temperature for 5 h, reduced in volume to *c.* 2 ml and treated with 50 ml of diethyl ether. The green solid was filtered off, washed with diethyl ether (2×10 ml), and vacuum dried; yield 0.036 g (85%). *Anal.* Calc. for $C_{50}H_{45}BCl_4F_4O_3P_4Re_2$: C, 42.32; H, 3.20. Found: C, 41.16; H, 3.16%.

The deprotonation of $[Re_2(\mu\text{-}OH)(O)_2Cl_4(\mu\text{-}dppm)_2]BF_4$

A quantity of **5** (0.05 g, 0.035 mmol) was dissolved in 4 ml of CH_2Cl_2 and this solution treated with less than an equivalent of triethylamine (1 ml of a 0.014 M solution in CH_2Cl_2, 0.014 mmol). The reaction mixture was stirred for 1 h and then treated with 50 ml of diethyl ether to precipitate a brown–green solid which was shown to be a mixture of **2a** and the compound $Re_2O_4Cl_2(dppm)_2$. The crude solid product was extracted into *c.* 15 ml of acetone, in which **2a** is more soluble than $Re_2O_4Cl_2(dppm)_2$, the extract reduced in volume to *c.* 3 ml, and diethyl ether added to precipitate a quantity of green $Re_2O_3Cl_4(dppm)_2$. A further quantity of **2a** was obtained by a similar work-up of the original reaction filtrate; combined yield 0.027 g (58%). The identity of this product as **2a** was established on the basis of its spectroscopic and electrochemical properties [1, 2].

When this deprotonation reaction was carried out in the presence of larger stoichiometric quantities of triethylamine the predominant product was the tetraoxo complex $Re_2O_4Cl_2(dppm)_2$, which is formed from the reaction of **2a** with the excess triethylamine that is present [3].

X-ray crystallography

Crystals of compositions $ReOCl_3(dppmO)\cdot CH_2Cl_2$ (**3**) and $Re_2OCl_6(dppm)_2$ (**4**) were grown by the diffusion of diisopropyl ether into dichloromethane solutions of the complexes. The structures of these crystals were determined by the application of standard procedures. The basic crystallographic parameters for the complexes are listed in Table 1. The cell constants are based on 25 reflections with $21 < \theta < 23°$ for **3** and $17 < \theta < 21°$ for **4**. The crystal of **3** was found to belong to the monoclinic space group $P2_1/n$ (No. 14); that of **4** to the orthorhombic space group *Pbca* (No. 61). Three standard reflections were measured after every 5000 s of beam exposure during data collection. There were no systematic variations in intensity. Lorentz and polarization corrections were applied to both data sets. An empirical absorption correction [5] was applied in each case. The linear absorption coefficient used was 48.92 cm^{-1} for **3** and 55.47 cm^{-1} for **4**. No corrections for extinction were applied. Calculations were performed on a micro VAX II computer using the Enraf-Nonius structure determination package.

The structures were solved by use of the Enraf-Nonius structure solution procedure MolEN and refined by full-matrix least-squares where the function minimized was $\Sigma w(|F_o|-|F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(F_o)$. The hydrogen atoms of the dppm ligands were included at fixed positions with $B(H) = 1.3B(C)$. The non-hydrogen atoms of the rhenium complexes were refined anisotropically; corrections

TABLE 1. Crystallographic data and data collection parameters for $ReOCl_3(dppmO)\cdot CH_2Cl_2$ (3) and $Re_2OCl_6(dppm)_2$ (4)

	3	4
Formula	$ReCl_5P_2O_2C_{26}H_{24}$	$Re_2Cl_6P_4OC_{50}H_{44}$
Formula weight	793.89	1369.92
Space group	$P2_1/n$ (No. 14)	*Pbca* (No. 61)
a (Å)	10.0440(8)	15.087(1)
b (Å)	15.821(1)	17.878(4)
c (Å)	18.082(2)	18.015(3)
β (°)	91.994(7)	
V (Å^3)	2871.6(7)	4859(2)
Z	4	4
D_c (g cm^{-3})	1.836	1.872
Crystal dimensions (mm)	0.43×0.31×0.25	0.22×0.19×0.05
Temperature (°C)	20	20
Radiation (wavelength)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
Monochromator	graphite	graphite
Linear absorption coefficient (cm^{-1})	48.92	55.47
Absorption correction applied	empirical[a]	empirical[a]
Transmission factors: min., max.	0.75, 1.00	0.69, 1.00
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Scan method	ω–2θ	ω–2θ
h, k, l limits	−10 to 10, 0 to 17, 0 to 19	0 to 16, 0 to 19, 0 to 19
2θ Range (°)	4.00–45.00	4.00–45.00
Scan width (°)	$0.45+0.35\tan(\theta)$	$0.39+0.35\tan(\theta)$
Take-off angle (°)	2.95	2.95
Programs used	Enraf-Nonius MolEN	Enraf-Nonius MolEN
$F(000)$	1544.0	2656.0
p-Factor used in weighting	0.040	0.040
Data collected	3913	3570
Unique data	3913	3570
Data with $I > 3.0\sigma(I)$	3177	2110
No. variables	325	286
Largest shift/e.s.d. in final cycle	0.08	0.04
R[b]	0.025	0.029
R_w[c]	0.037	0.034
GOF[d]	1.181	0.824

[a] See ref 5. [b] $R = \Sigma||F_o|-|F_c||/\Sigma|F_o|$. [c] $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(F_o)$ [d] Goodness of fit $= [\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{parameters})]^{1/2}$.

for anomalous scattering were applied to these atoms [6]. The final residuals for **3** were $R = 0.025$ ($R_w = 0.037$) for 3177 data with $I > 3\sigma(I)$, while for **4** we have $R = 0.029$ ($R_w = 0.034$) for 2110 data with $I > 3\sigma(I)$.

Tables 2 and 3 list the atomic positional parameters and their errors for the non-hydrogen atoms, while Tables 4 and 5 provide the more important intramolecular bond distances and angles for the two structures. See also 'Supplementary material'.

Physical measurements

A Perkin-Elmer 1800 FTIR spectrometer was used to record the IR spectra of the compounds as mineral oil (Nujol) mulls. Electrochemical measurements were carried out on dichloromethane solutions that contained 0.1 M tetra-n-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a}+E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at room temperature and are uncorrected for junction potentials. Under our experimental conditions $E_{1/2} = +0.47$ V versus Ag/AgCl for the ferrocenium/ferrocene couple. Voltammetric experiments were performed with a BAS Inc. model CV-27 instrument in conjunction with a BAS model RXY recorder. NMR spectra were recorded on CD_2Cl_2 or $CDCl_3$ solutions of the compounds. The $^{31}P\{^1H\}$ spectra were obtained with use of a Varian XL-200A spectrometer operated at 80.98 MHz with 85% H_3PO_4 as an external standard. ^1H NMR spectra were obtained on a GE QE-300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent.

TABLE 2. Positional parameters for non-hydrogen atoms of **3** and their e.s.d.s[a]

Atom	*x*	*y*	*z*	*B* (Å²)
Re	0.08682(2)	0.04252(2)	0.28295(1)	2.641(5)
Cl(1)	0.0878(2)	−0.0126(1)	0.40476(9)	3.72(4)
Cl(2)	0.1380(2)	0.1062(1)	0.16908(9)	4.48(4)
Cl(3)	0.1349(2)	0.1752(1)	0.3363(1)	4.04(4)
P(11)	0.3765(2)	−0.0588(1)	0.28994(9)	2.72(3)
P(12)	0.1064(2)	−0.1013(1)	0.23416(8)	2.64(3)
O(1)	−0.0784(4)	0.0381(3)	0.2681(3)	4.3(1)
O(11)	0.2957(4)	0.0216(3)	0.2945(2)	2.93(9)
C(1B)	0.2596(6)	−0.1438(4)	0.2773(3)	3.1(1)
C(1111)	0.4797(6)	−0.0781(4)	0.3705(3)	3.0(1)
C(1112)	0.4429(7)	−0.1302(6)	0.4262(4)	5.3(2)
C(1113)	0.5232(8)	−0.1412(6)	0.4889(4)	5.7(2)
C(1114)	0.6397(7)	−0.0990(5)	0.4968(4)	4.6(2)
C(1115)	0.6812(8)	−0.0470(5)	0.4408(5)	5.2(2)
C(1116)	0.6020(8)	−0.0365(4)	0.3777(4)	4.3(2)
C(1121)	0.4801(6)	−0.0534(4)	0.2121(3)	3.0(1)
C(1122)	0.4704(7)	0.0144(5)	0.1645(4)	4.1(2)
C(1123)	0.5470(8)	0.0163(6)	0.1027(4)	5.3(2)
C(1124)	0.6329(8)	−0.0483(6)	0.0894(5)	5.3(2)
C(1125)	0.6421(7)	−0.1156(5)	0.1355(4)	4.6(2)
C(1126)	0.5656(7)	−0.1195(4)	0.1968(4)	3.8(2)
C(1211)	0.1163(6)	−0.1118(4)	0.1348(3)	3.0(1)
C(1212)	0.0022(7)	−0.0926(6)	0.0936(4)	4.8(2)
C(1213)	−0.0021(8)	−0.1024(6)	0.0179(4)	5.5(2)
C(1214)	0.1072(8)	−0.1304(6)	−0.0171(4)	5.2(2)
C(1215)	0.2219(7)	−0.1474(5)	0.0236(4)	4.5(2)
C(1216)	0.2262(7)	−0.1391(4)	0.0987(4)	3.6(1)
C(1221)	−0.0197(6)	−0.1776(4)	0.2572(3)	3.1(1)
C(1222)	−0.1150(6)	−0.1612(4)	0.3093(4)	3.6(1)
C(1223)	−0.2066(7)	−0.2216(5)	0.3262(4)	4.6(2)
C(1224)	−0.2067(8)	−0.2982(5)	0.2915(5)	5.4(2)
C(1225)	−0.112(1)	−0.3159(5)	0.2410(5)	6.1(2)
C(1226)	−0.0177(9)	−0.2555(5)	0.2242(4)	4.8(2)
Cl(1001)	0.3797(3)	0.2288(2)	0.0557(1)	7.00(6)
Cl(1002)	0.3057(3)	0.3321(2)	−0.0707(2)	7.47(6)
C(1000)	0.4349(9)	0.2984(6)	−0.0127(5)	6.1(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3)-$[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

TABLE 3. Positional parameters for non-hydrogen atoms of **4** and their e.s.d.s[a]

Atom	*x*	*y*	*z*	*B* (Å²)
Re	0.42038(2)	−0.01153(2)	0.57580(2)	1.868(6)
Cl(1)	0.4455(2)	−0.1419(1)	0.5696(1)	3.11(5)
Cl(2)	0.3924(2)	0.3830(1)	0.0887(1)	3.19(5)
Cl(3)	0.3166(2)	−0.0348(2)	0.6699(1)	3.96(6)
P(1)	0.3016(1)	−0.0043(1)	0.4784(1)	1.96(5)
P(2)	0.4443(1)	0.0064(1)	0.3440(1)	2.01(5)
O(B)	0.5	0	0.5	1.2(1)
C(B)	0.3504(6)	0.0434(5)	0.3982(5)	2.2(2)
C(111)	0.2097(5)	0.0585(5)	0.4994(5)	2.0(2)
C(112)	0.2125(6)	0.1338(5)	0.4838(5)	2.6(2)
C(113)	0.1429(6)	0.1800(5)	0.5036(5)	2.6(2)
C(114)	0.0710(6)	0.1514(5)	0.5387(5)	3.3(2)
C(115)	0.0663(6)	0.0768(6)	0.5550(5)	3.2(2)
C(116)	0.1352(6)	0.0298(5)	0.5365(5)	2.8(2)
C(121)	0.2421(6)	−0.0855(5)	0.4454(5)	2.4(2)
C(122)	0.2018(6)	−0.0855(6)	0.3751(6)	3.3(2)
C(123)	0.1503(7)	−0.1455(6)	0.3526(7)	4.5(3)
C(124)	0.1373(7)	−0.2035(6)	0.4008(8)	5.8(3)
C(125)	0.1729(7)	−0.2029(6)	0.4714(7)	4.6(3)
C(126)	0.2276(7)	−0.1445(6)	0.4936(6)	4.1(3)
C(211)	0.4036(5)	−0.0811(5)	0.3053(5)	2.0(2)
C(212)	0.4085(6)	−0.1467(5)	0.3467(5)	3.0(2)
C(213)	0.3748(7)	−0.2129(5)	0.3188(7)	3.9(2)
C(214)	0.3344(7)	−0.2136(6)	0.2505(7)	4.4(2)
C(215)	0.3275(8)	−0.1503(6)	0.2095(6)	4.5(3)
C(216)	0.3615(7)	−0.0838(5)	0.2360(5)	2.9(2)
C(221)	0.4481(6)	0.0698(5)	0.2650(5)	2.2(2)
C(222)	0.3954(7)	0.1335(5)	0.2575(6)	3.4(2)
C(223)	0.4032(7)	0.1769(6)	0.1941(6)	4.5(3)
C(224)	0.4616(7)	0.1583(6)	0.1400(6)	4.0(2)
C(225)	0.5142(7)	0.0964(6)	0.1480(5)	3.4(2)
C(226)	0.5087(6)	0.0537(6)	0.2096(5)	3.1(2)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as (4/3)-$[a^2\beta(1,1)+b^2\beta(2,2)+c^2\beta(3,3)+ab(\cos\gamma)\beta(1,2)+ac(\cos\beta)\beta(1,3)+bc(\cos\alpha)\beta(2,3)]$.

TABLE 4. Some important bond distances (Å) and bond angles (°) for **3**[a]

Bond distances			
Re–Cl(1)	2.369(2)	Re–O(11)	2.127(4)
Re–Cl(2)	2.364(2)	P(11)–O(11)	1.513(4)
Re–Cl(3)	2.354(2)	P(11)–C(1B)	1.795(7)
Re–P(12)	2.450(2)	P(12)–C(1B)	1.829(6)
Re–O(1)	1.673(5)		
Bond angles			
Cl(1)–Re–Cl(2)	166.55(6)	Cl(3)–Re–O(1)	106 9(2)
Cl(1)–Re–Cl(3)	87.32(6)	Cl(3)–Re–O(11)	84.9(1)
Cl(1)–Re–P(12)	89.72(6)	P(12)–Re–O(1)	89.7(2)
Cl(1)–Re–O(1)	96.1(2)	P(12)–Re–O(11)	78.5(1)
Cl(1)–Re–O(11)	83.1(1)	O(1)–Re–O(11)	168.1(2)
Cl(2)–Re–Cl(3)	85.95(7)	O(11)–P(11)–C(1B)	106.7(3)
Cl(2)–Re–P(12)	93.39(6)	Re–P(12)–C(1B)	105.3(2)
Cl(2)–Re–O(1)	97.0(2)	Re–O(11)–P(11)	130.9(3)
Cl(2)–Re–O(11)	84.7(1)	P(11)–C(1B)–P(12)	108 4(3)
Cl(3)–Re–P(12)	163.31(6)		

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 5. Some important bond distances (Å) and bond angles (°) for **4**[a]

Bond distances			
Re–Cl(1)	2.363(2)	Re–P(1)	2.511(2)
Re–Cl(2)	2.348(2)	Re–P(2)	2.502(2)
Re–Cl(3)	2.345(3)	Re–O(B)	1.8303(3)
Bond angles			
Cl(1)–Re–Cl(2)	176.8(1)	Cl(2)–Re–O(B)	94.69(7)
Cl(1)–Re–Cl(3)	88.1(1)	Cl(3)–Re–P(1)	92.17(9)
Cl(1)–Re–P(1)	97.57(9)	Cl(3)–Re–P(2)	97.69(9)
Cl(1)–Re–P(2)	86.15(8)	Cl(3)–Re–O(B)	176.00(8)
Cl(1)–Re–O(B)	88.30(6)	P(1)–Re–P(2)	169.58(8)
Cl(2)–Re–Cl(3)	89.0(1)	P(1)–Re–O(B)	86.62(5)
Cl(2)–Re–P(1)	83.72(9)	P(2)–Re–O(B)	83.75(5)
Cl(2)–Re–P(2)	93 08(8)	Re–O(B)–Re	180.0

[a]Numbers in parentheses are e.s.d.s in the least significant digits.

Elemental microanalyses were performed by Dr H.D. Lee of the Purdue University Microanalytical Laboratory.

Results and discussion

Oxygenation of $Re_2(\mu\text{-}O)(O)_2Cl_4(\mu\text{-}dppm)_2$

The reaction of the dirhenium(II) compound $Re_2Cl_4(\mu$-dppm$)_2$ with O_2 in a variety of solvents affords the dirhenium(V) complex $Re_2(\mu$-O)(O$)_2Cl_4(\mu$-dppm$)_2$ (**2a**) via the intermediacy of the unsymmetrical complex $Re_2(\mu$-O)(μ-Cl)(O)$Cl_3(\mu$-dppm$)_2$ (**1a**). In the present study we find that when **2a** is reacted further with O_2 in tetrahydrofuran the mononuclear species ReOCl_3(dppmO) (**3**), where dppmO represents the mixed phosphine–phosphine oxide ligand $Ph_2PCH_2P(O)Ph_2$, is formed in moderate yield after a reaction period of *c.* 30 h. We do not know the fate of the remaining rhenium and, therefore, the stoichiometry of the reaction. Compound **1a** also converts to **3** under these same reaction conditions but this reaction proceeds through **2a**. The synthesis of **3** is more conveniently approached by the reaction of **2a** (or **1a**) with any of the peroxy compounds Bu^{t}OOH, H_2O_2 or *m*-chloroperbenzoic for 2–3 h. The yields are significantly higher by this procedure. For example, the yield is 65% in the case of the reaction of **2a** with ^{t}BuOOH; we assume that only one-half of the rhenium in **2a** can end up as **3** because of the deficiency of Cl in the starting complex **2a**. Following the completion of this work, and just prior to the submission of this manuscript for publication, a report appeared [7] describing the preparation of $ReOCl_3$(dppmO) from the reaction between $[ReOCl_4]^-$ and $Ph_2P(O)CH_2PPh_2$.

The mononuclear complex **3** shows a ν(Re=O) mode at 987(s) cm^{-1} in its Nujol mull IR spectrum and a band at 1125(s) cm^{-1} assigned to ν(P=O) of the chelating η^2-dppmO ligand. Its ^{1}H NMR spectrum (recorded in CD_2Cl_2) is very simple, with a doublet of doublets at $\delta+4.01$ (2H), assigned to the $-CH_2-$ group of the dppmO ligand, and multiplets at $\delta+7.39$, $+7.52$ and $+7.62$ (20H) due to the phenyl rings. The $^{31}P\{^1H\}$ NMR spectrum in CD_2Cl_2 consists of doublets at $\delta+58.6$ and $\delta\ -16.3$ (J(P–P)$=16$ Hz) due to the phosphine oxide and phosphine P atoms. The aforementioned spectroscopic properties are very similar to those reported for a sample of **3** prepared from mononuclear $[ReOCl_4]^-$ [7]. The electrochemical properties of **3**, as measured by the cyclic voltammetric technique on a solution in 0.1 M TBAH–CH_2Cl_2, comprise an oxidation at $E_{1/2}=+1.48$ V and a reduction at $E_{1/2}=-0.74$ V versus Ag/AgCl. With a sweep rate of 200 mV s^{-1}, $i_{p,a}\approx i_{p,c}$ for both couples and ΔE_p ($E_{p,a}-E_{p,c}$) was equal to 80 mV ($E_{1/2}$(ox)) and 120 mV ($E_{1/2}$(red)).

The crystal structure determination of **3** was carried out on a crystal of composition $ReOCl_3$(dppmO)$\cdot CH_2Cl_2$. An ORTEP representation of the rhenium containing molecule is shown in Fig. 1, in which the phenyl group atoms have been omitted for clarity. The

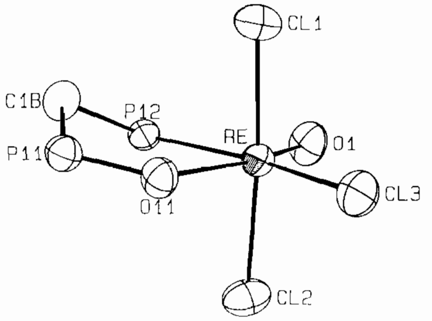

Fig 1. ORTEP representation of the structure of the ReOCl_3(dppmO) molecule (**3**) with the phenyl group atoms omitted. The thermal ellipsoids are drawn at the 50% probability level.

important crystallographic and structural parameters are given in Tables 1, 2 and 4. The structure of the rhenium complex in $ReOCl_3(dppmO) \cdot CH_2Cl_2$ is very similar to that in a crystal of composition $ReOCl_3(dppmO) \cdot 0.5THF$ [7]; the latter contains two crystallographically independent molecules of $ReOCl_3(dppmO)$ in the asymmetric unit. The geometry approximates to octahedral with the angles O(1)–Re–O(11), Cl(1)–Re–Cl(2) and Cl(3)–Re–P(12) being in the range 163.3–168.1°. Their deviation from linearity reflects in part the expected displacement of the terminal Re=O unit out of the plane defined by Cl(1), Cl(2), Cl(3) and P(12). The Re–O(1) distance (1.673(5) Å) is typical for a terminal Re=O bond in a mononuclear $[ReO]^{3+}$ complex [8, 9]. Most noteworthy is the stable, puckered, five-membered ring $\overline{\text{Re–O(11)–P(11)–C(1B)–P(12)}}$ which is formed following oxidation of the dppm ligand to dppmO. The torsional angle O(11)–P(11)–C(1B)–P(12) is 25.3(4)°. The complex $ReCl_3(dppm)(dppmO)$ has recently been prepared and structurally characterized [10], but contains a dangling dppmO ligand in which the P=O unit is free. In this compound the P=O bond length of 1.485(7) Å is shorter than that in **3** (1.513(4) Å), although within the limits of 3σ this measured difference may not be significant.

Compound **3** was also prepared during attempts to access the one-electron oxidation of **1a** at $E_{1/2} = +0.47$ V versus Ag/AgCl [1] through the use of $NOPF_6$ as oxidant. Rather than generating the paramagnetic cation $[\textbf{1a}]^+$, the mononuclear complex **3** was isolated as the major identifiable product of this reaction, signifying that $[\textbf{1a}]^+$, if formed, is not stable under these conditions. Interestingly, when $[(\eta^5\text{-}C_5H_5)_2Fe]PF_6$, which has $E_{1/2} = +0.47$ V for the ferrocenium/ferrocene couple (i.e. identical to the $E_{1/2}$ value for the $[\textbf{1a}]^+/\textbf{1a}$ couple), was used in place of $NOPF_6$ a quite different product was isolated. A gray–green solid was obtained which is also formed when $(C_7H_7)PF_6$ or $(Ph_3C)PF_6$ are reacted with **1a** in deoxygenated CH_2Cl_2. We have also encountered it on several occasions as a minor product in other reactions. However, its identity remains uncertain at this time and this product is under further study. Some of its more important properties are included in 'Experimental'.

Protonation of $Re_2(\mu\text{-}O)(O)_2Cl_4(\mu\text{-}dppm)_2$

The treatment of **2a** with $HBF_4 \cdot Et_2O$ produces a green solid in high yield which we formulate as the μ-hydroxy complex $[Re_2(\mu\text{-}OH)(O)_2Cl_4(\mu\text{-}dppm)_2]BF_4$ (**5**). A solution of **5** in acetone (1.0×10^{-3} M) possesses a conductivity characteristic of a 1:1 electrolyte ($\Lambda_m = 95$ ohm^{-1} cm^2 mol^{-1}). The Nujol mull IR spectrum of this product shows ν(Re=O) at 967(m) cm^{-1} and ν(B–F) for the $[BF_4]^-$ anion at 1064(s) cm^{-1}. The cyclic voltammogram of a solution of **5** in 0.1 M TBAH–CH_2Cl_2 is quite different from that of **2a** [1] and shows a single reduction at $E_{p,c} = -0.36$ V versus Ag/AgCl. With a sweep rate of 200 mV s^{-1} the coupled oxidation wave is found at -0.12 V but with $i_{p,a} < i_{p,c}$. The ^1H NMR spectrum of **5** consists of a group of well resolved phenyl proton resonances between $\delta + 7.9$ and $+7.2$ and an ABX_4 pattern for the $-CH_2-$ groups of the dppm ligands with multiplets centered at δ +4.05 and +3.57. We did not observe a resonance that could be attributed to the μ-OH group, although the IR spectrum of **5** did display a broad ν(OH) mode at *c*. 3300 cm^{-1}. The $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) was a singlet at δ −17.9.

When **5** is treated with a base such as NEt_3 deprotonation occurs to regenerate **2a**, which in the presence of an excess of the base will convert to the tetraoxo complex $Re_2(\mu\text{-}O)_2(O)_2Cl_2(\mu\text{-}dppm)_2$ [3]. This conversion can be followed conveniently by $^{31}P\{^1H\}$ NMR spectroscopy through the appearance of resonances at δ −14.5 (for **2a** [1]) and δ −24.5 (for $Re_2O_4Cl_2(dppm)_2$ [3]).

Reaction of $Re_2(\mu\text{-}O)(\mu\text{-}Cl)(O)Cl_3(\mu\text{-}dppm)_2$ with thionyl chloride

Thionyl chloride is an effective reagent for converting an M=O unit to MCl_2 [11]. In the present study, we have found that **1a** reacts with $SOCl_2$ to afford the corner-sharing bioctahedral complex $Re_2(\mu\text{-}O)Cl_6(\mu\text{-}dppm)_2$ (**4**) according to the stoichiometry shown in eqn. (1):

$$Re_2O_2Cl_4(dppm)_2 + SOCl_2 \longrightarrow Re_2OCl_6(dppm)_2 + SO_2 \quad (1)$$

The structure of a crystal of **4** was determined by X-ray crystallography (Fig. 2). The dirhenium complex possesses a crystallographically imposed inversion center and is essentially isostructural with the diosmium(IV) analogue $Os_2(\mu\text{-}O)Cl_6(\mu\text{-}dppm)_2$ [12]. The Re–O distance of 1.8303(3) Å is, as expected, slightly longer than the distance of 1.792(1) Å reported for $Os_2(\mu\text{-}O)Cl_6(\mu\text{-}dppm)_2$ [12] but very similar to the Re–O distances in $K_4Re_2(\mu\text{-}O)Cl_{10}$ (1.865(2) Å) [13]. However, the axial Re–Cl bonds, colinear with the Re–O–Re bridging unit, are not significantly different in length from the average of the equatorial Re–Cl bonds (2.355[8] Å), whereas in the diosmium(IV) complex the axial Os–Cl bonds are significantly shorter (2.307(3) Å) than the equatorial Os–Cl bonds (av. 2.374[14] Å).

In spite of the rather low solubility of **4** in CD_2Cl_2, a satisfactory ^1H NMR spectrum was obtained. This showed unusual chemical shifts for the dppm ligand protons, presumably due to the diamagnetic anisotropy effects associated with the Re–O–Re unit. The $-CH_2-$

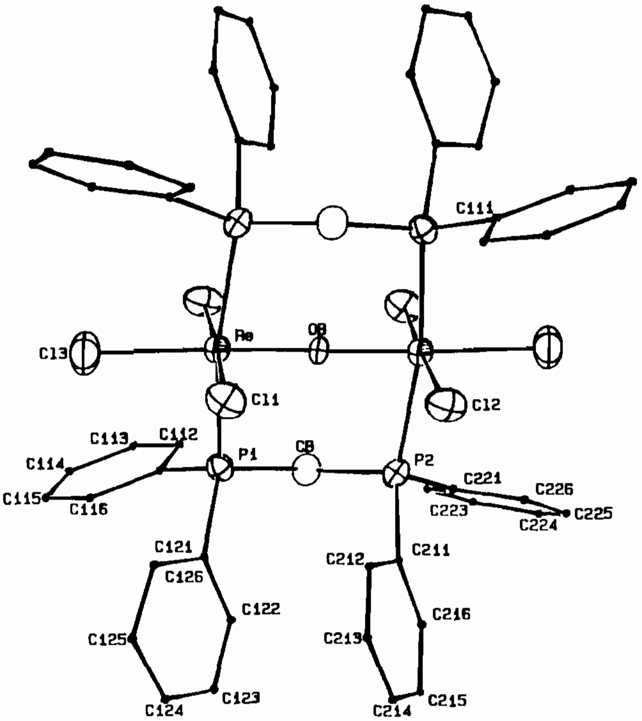

Fig. 2. ORTEP representation of the structure of the $Re_2(\mu\text{-}O)Cl_6(\mu\text{-dppm})_2$ molecule (**4**). The thermal ellipsoids are drawn at the 50% probability level except for the phenyl group atoms which are circles of arbitrary radius.

resonance is seen as a broad feature at δ −0.43 (4H), while the phenyl resonances consist of triplets at δ +7.30 (16H) and δ +7.49 (8H), and a doublet at δ +9.27 (16H).

A cyclic voltammogram of a solution of **4** in 0.1 M TBAH-CH_2Cl_2 shows a reversible one-electron oxidation at $E_{1/2} = +1.08$ V, and two reversible reductions at $E_{1/2} = -0.02$ and −0.88 V versus Ag/AgCl. For all three processes $i_{p,a} = i_{p,c}$, and the values of $\Delta E_p(E_{p,a} - E_{p,c})$ were in the range 110–90 mV when a sweep rate of 200 mV s^{-1} was used. These processes correspond to the redox couples $[Re_2O]^{7+}/[Re_2O]^{6+}$, $[Re_2O]^{6+}/[Re_2O]^{5+}$ and $[Re_2O]^{5+}/[Re_2O]^{4+}$, respectively. Interestingly, similar electrochemical responses are found in the cyclic voltammogram of $Os_2(\mu\text{-}O)Cl_6(\mu\text{-dppm})_2$ (recorded in 0.1 $Bu_4{}^nNClO_4$–CH_2Cl_2), with the $[Os_2O]^{7+}/[Os_2O]^{6+}$, $[Os_2O]^{6+}/[Os_2O]^{5+}$ and $[Os_2O]^{5+}/[Os_2O]^{4+}$ couples characterized by processes at $E_{1/2} = +1.62$ V, $E_{1/2} = +0.09$ V and $E_{p,c} = -1.13$ V versus SCE [12]. Of course, these two systems differ electronically, with the dirhenium species each possessing two electrons less than their similarly charged diosmium analogues. The four electrochemical processes observed for $Re_2(\mu\text{-}O)Cl_6(\mu\text{-dppm})_2$ involve oxidations and reductions that are associated with what are essentially non-bonding metal-based orbitals [12, 14, 15] thereby explaining their reversibility. Future studies will be directed towards the isolation and characterization of salts of these oxidized and/or reduced species.

While claims have been made previously for the isolation of neutral complexes of stoichiometry $Re_2OCl_6L_4$ (e.g. $L = Et_2S$ or $1/2(EtSCH_2CH_2SEt)$) [16], compound **4** constitutes the first structurally characterized species of this type.

Supplementary material

Tables of positional parameters for the hydrogen atoms, anisotropic thermal parameters, full listings of bond distances and bond angles, and observed and calculated structure factors for **3** and **4** are available on request from author R.A.W. Further details concerning the structure determination can be obtained from Dr P.E. Fanwick.

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